

Amorphization induced by pressure: results for zeolites and general implications

Inmaculada Peral^{1,2,3} and Jorge Íñiguez^{1,3}

¹*Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, 08193 Bellaterra, Spain*

²*Departament de Física, Universitat Autònoma de Barcelona, 08193 Bellaterra, Spain*

³*NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*

We report an *ab initio* study of pressure-induced amorphization (PIA) in zeolites, which are model systems for this phenomenon. We confirm the occurrence of low-density amorphous phases like the one reported by Greaves *et al.* [Science **308**, 1299 (2005)], which preserves the crystalline topology and might constitute a new type of glass. The role of the zeolite composition regarding PIA is explained. Our results support the correctness of existing models for the basic PIA mechanism, but suggest that energetic, rather than kinetic, factors determine the irreversibility of the transition.

PACS numbers: 61.50.Ks, 61.43.Fs, 64.70.Pf, 82.75.-z

Many minerals can be turned amorphous by mere application of pressure, an intriguing phenomenon known as pressure induced amorphization (PIA) [1]. The concrete realizations of PIA can be quite diverse. Remarkably, upon release of the applied pressure some materials recover their crystalline order, thus exhibiting reversible amorphization, while others remain amorphous. Our understanding of PIA is only partial. Simulations of systems like α -quartz [2], silica [3], and α -berlinite [4] suggest PIA is the result of a first-order transition associated with very localized, weakly interacting structural distortions that become unstable upon compression. In such a transition, domain nucleation would overwhelm growth and destroy the long-range order [5]. Cohen, Íñiguez and Neaton [5] (CIN) further propose the PIA transition will be reversible if the crystalline *topology* is preserved in the amorphous phase, i.e., if the amorphization does not involve bond formation or breaking. While physically plausible, this picture is yet to be confirmed.

The recent work of Greaves *et al.* [6] on the nanoporous aluminosilicates known as zeolites has renewed the interest in PIA. These authors have shown a zeolite may present two distinct PIA phases: a low-pressure (≈ 2 GPa) low-density amorphous phase (LDA), which they argue may constitute a new type of glass, and a high-pressure (≈ 6 GPa) high-density amorphous phase (HDA). Further, they claim the crystalline topology is preserved in the LDA phase and lost in the HDA phase, which, according to the CIN picture, implies amorphization will be reversible in the former case and irreversible in the latter. These results, together with other studies [7, 8] that, for example, show a striking dependence of the PIA reversibility on the zeolite composition, clearly point at these systems as ideal to test general PIA theories.

Here we present an *ab initio* study of PIA in three representative zeolites with different compositions. Our results (i) confirm the occurrence of the above mentioned LDA and HDA phases, (ii) show how the zeolite composition controls the nature of the PIA transition, and (iii) essentially confirm, and perfect, the CIN picture regarding PIA reversibility. While obtained for zeolites, our

results clearly pertain PIA phenomena at large.

We used the Generalized Gradient Approximation to Density Functional Theory [9] as implemented in the code SIESTA [10]. Note that we wanted to study amorphization occurring in spite of negligible thermal activation, and thus focused on low temperature simulations. We proceeded as follows: at each considered pressure, we performed a short (100 fs) molecular dynamics simulation at 100 K, starting with random velocities, and relaxed the resulting structure. Zeolites have the general formula $A_{x/n}^{n+}Al_xSi_{1-x}O_2$, where A is a charge-compensating cation (e.g. Li or Na). The Si and Al atoms are at the center of corner-sharing O_4 tetrahedra. A typical zeolite structure, with the so-called LTA framework, is sketched in the top-right inset of Fig. 1; note the four-, double-four-, six-, and eight-member rings (denoted as 4MR's, D4R's, etc.), also known as *secondary building units*. We studied three LTA zeolites with different percentages of Al and Na as the charge-compensating cation: an Al-free "all-SiO₂" system, Na-ZK4 with a 1-to-5 Al-Si ratio, and Na-A where the ratio is 1-to-1. Following experimental information [11], we considered primitive cells containing 72, 76, and 168 atoms, respectively, for all-SiO₂, Na-ZK4, and Na-A.

All-SiO₂ results.— The all-SiO₂ LTA zeolite exhibits most of our key findings. Figure 1 shows the pressure dependence of the unit cell volume and the evolution of an 8MR that captures the typical structural distortions. The slope changes and volume discontinuities indicate a series of phase transitions. It is sufficient for our purposes to describe the structure in terms of the average values and standard deviations of the relevant angles (Si–O–Si and O–Si–O) and distances (Si–O). For example, for the reference LTA structure at 0 GPa we obtained $\bar{d}_{SiO}=1.63\pm0.01$ Å, $\bar{\theta}_{OSiO}=109\pm1^\circ$, and $\bar{\theta}_{SiOSi}=151\pm8^\circ$.

Phases I to III in Fig. 1 are connected by continuous transitions characterized by rigid rotations of the O_4 tetrahedra. Such Rigid Unit Modes (RUM's [12]) are mainly reflected in $\bar{\theta}_{SiOSi}$. For example, for phase III at 2.75 GPa we obtained $\bar{d}_{SiO}=1.62\pm0.01$ Å, $\bar{\theta}_{OSiO}=109\pm2^\circ$, and $\bar{\theta}_{SiOSi}=142\pm18^\circ$. At 3.5 GPa

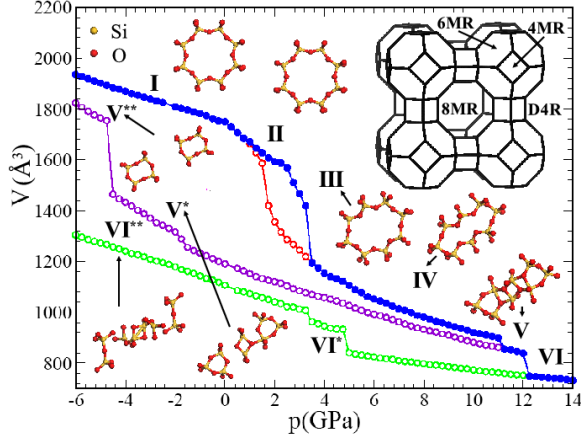


FIG. 1: Pressure dependence of the all-SiO₂ unit cell volume. Solid and open symbols refer, respectively, to compression and decompression. Also shown is the evolution of a representative eight-member ring. The top-right inset is a sketch of the LTA-framework structure as defined by the Si/Al atoms.

phase III transforms discontinuously into a phase IV of significantly smaller volume. This transition does not involve any topological change, i.e. no bonds are formed or broken. In fact, as in the previous cases, the structural changes mostly affect $\bar{\theta}_{\text{SiOSi}}$; at 7 GPa we obtained: $\bar{d}_{\text{SiO}}=1.63\pm0.02$ Å, $\bar{\theta}_{\text{OSiO}}=109\pm7^\circ$, and $\bar{\theta}_{\text{SiOSi}}=132\pm20^\circ$.

At 11.25 GPa phase IV transforms discontinuously into a phase V, and at 12.25 GPa there is another first-order transition to a phase VI. Phases V and VI display collapsed rings of all types and new Si–O bonds (see the 8MR depicted in Fig. 1), with the corresponding loss of the LTA-framework topology. The occurrence of SiO₅ and SiO₆ groups results in a wide dispersion of distances and angles. For example, at 13 GPa we obtained $\bar{d}_{\text{SiO}}=1.70\pm0.10$ Å, $\bar{\theta}_{\text{OSiO}}=107\pm23^\circ$, and $\bar{\theta}_{\text{SiOSi}}=117\pm17^\circ$. Note the increase in the average Si–O distance, which reflects the existence of high-coordination defects.

Figure 1 also shows our results regarding the reversibility of the transitions. The transitions to phases II and III are reversible, with no hysteresis in the $V(p)$ curve. Phase IV can also transform back to the crystalline phase, but hysteresis occurs in this case. Note that the presence or absence of hysteresis agrees with the observed character, first- or second-order, of the transition. Finally, upon decompression from phases V and VI, the system undergoes a number of structural changes but does not find its way back to the low-pressure stable phases. The transitions to phases V and VI are thus irreversible.

Our simulations reveal the atomistic origin of this irreversibility. The metastable phases V** and VI** in Fig. 1 present the right first-neighbor coordination and can thus be viewed as formed by SiO₄ units. However, the ring structure is not the LTA one. For example, in phase V**

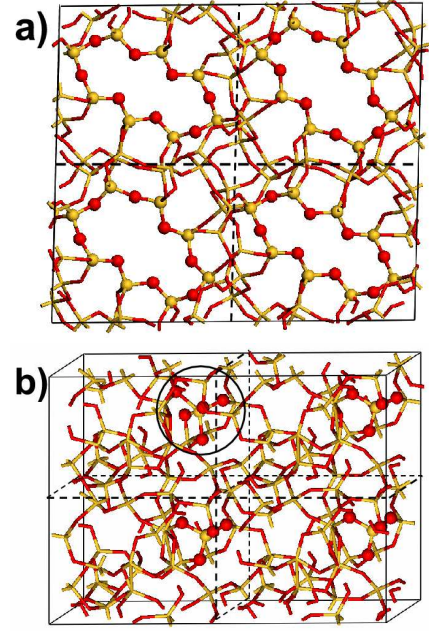


FIG. 2: All-SiO₂ $2\times2\times1$ supercells (see text) resulting from transitions at 3.50 GPa (panel a) and 11.25 GPa (panel b). Dashed lines sketch the cell we start from. We highlight examples of atoms that were translationally related before the transition; a SiO₅ group is circled in panel b.

the original 8MR has transformed into two disconnected 4MR's, and phases V* and VI** contain Si pairs sharing two oxygens (see Fig. 1). Note that phases V** and VI** are robustly metastable: while their excess energy with respect to phase I is relatively large (about 0.35 eV per formula unit at 0 GPa), a transition to the crystalline phase would require multiple Si–O bond breakings within SiO₄ units, which is energetically very costly.

The origin of the defects affecting the ring topology can be easily identified. Phases V and VI exhibit collapsed rings in which bonds form between Si and O atoms on opposite sides of the original rings. The resulting SiO₅ and SiO₆ groups break upon decompression, and the atoms recover their original coordination. However, this defect breaking can happen in a variety of ways from which *only one* allows the ring to fully recover at low pressures. In addition, this unique *right* way involves the largest volume expansion and, thus, is energetically favorable only at relatively low pressures. For example, for phase VI we obtained that above 2 GPa the SiO₅ and SiO₆ groups find it energetically favorable to break in ways that restore the original atomic coordination but, at the same time, destroy the 8MR.

We also investigated if these transitions involve true amorphization. Our simulated system is defined by the unit cell of the LTA structure and, thus, cannot capture the translational symmetry breaking characterizing amorphization. Hence, in a few selected cases we consid-

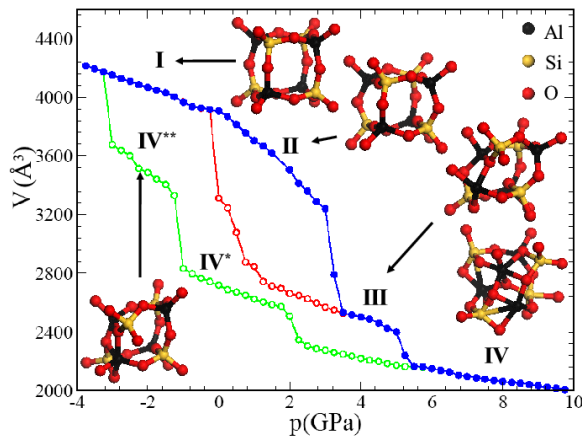


FIG. 3: Same as Fig. 1 for the Na-A zeolite.

ered larger supercells and simulated the loss of translational symmetry directly. More precisely, we considered the relaxed structures obtained at pressures neighboring transition points (i.e. 0 GPa, 3.5 GPa, etc.), created the corresponding $2 \times 2 \times 1 \times 72$ -atom supercells, and increased the pressure to observe how the transformation proceeds. Interestingly, for the second-order transitions to phases II and III, the translations within the supercell are preserved, indicating that no PIA occurs. On the other hand, as shown in Fig. 2, the translational symmetry within the supercell is completely lost in the transitions to phases IV and V, both of which are first-order in character. We can thus conclude that phases IV and V are genuine amorphous phases, the crystal topology being preserved in the former and lost in the latter.

Na-ZK4 and Na-A results.— We consider first the case of Na-A, which is more informative. Figure 3 shows the pressure dependence of the 168-atom primitive cell and the evolution of a D4R, which captures the typical structural distortions. (Note that the Si and Al atoms are intercalated in Na-A.) Phase I is the reference phase, which at 0 GPa is characterized by $\bar{d}_{\text{SiO}} = 1.65 \pm 0.01$ Å, $\bar{d}_{\text{AlO}} = 1.76 \pm 0.02$ Å, $\bar{\theta}_{\text{OSiO}} = 109 \pm 5^\circ$, $\bar{\theta}_{\text{OAlO}} = 109 \pm 3^\circ$, and $\bar{\theta}_{\text{SiOAl}} = 148 \pm 10^\circ$. Phases II and III are the product of two transitions that are, respectively, continuous and discontinuous. Both transformations are characterized by RUM's that involve rotations of the O_4 tetrahedra and mainly affect the Si-O-Al angles. For example, for phase III at 5 GPa we obtained $\bar{d}_{\text{SiO}} = 1.66 \pm 0.05$ Å, $\bar{d}_{\text{AlO}} = 1.82 \pm 0.09$ Å, $\bar{\theta}_{\text{OSiO}} = 109 \pm 10^\circ$, $\bar{\theta}_{\text{OAlO}} = 108 \pm 21^\circ$, and $\bar{\theta}_{\text{SiOAl}} = 118 \pm 18^\circ$. Note that phase III preserves the LTA topology, clearly resembling what we found for phase IV of all-SiO₂.

At about 5.25 GPa the system undergoes a second discontinuous transition to a phase IV in which the D4R's collapse and the LTA topology is lost. Comparison with all-SiO₂ clearly suggests the presence of Al reduces the pressure at which the coordination defects appear, which

is consistent with the fact that Al is more likely than Si to have a 5- or 6-fold oxygen coordination. Note also that only the D4R's collapse in phase IV. Interestingly, in Na-A the centers of all the 6 and 8MR's are occupied by Na atoms, which suggests that the cations are responsible for the preservation of the large rings. The structure of phase IV at 7 GPa is characterized by $\bar{d}_{\text{SiO}} = 1.67 \pm 0.06$ Å, $\bar{d}_{\text{AlO}} = 1.85 \pm 0.10$ Å, $\bar{\theta}_{\text{OSiO}} = 109 \pm 12^\circ$, $\bar{\theta}_{\text{OAlO}} = 107 \pm 24^\circ$, and $\bar{\theta}_{\text{SiOAl}} = 116 \pm 20^\circ$. The relatively large standard deviations reflect the structural disorder.

As shown in Fig. 3, we found that *all* the transitions in Na-A are reversible. Hysteresis does not occur in the case of the second-order transition (to phase II), but it does for the first-order transitions (to phases III and IV). Note that the reversibility from phases II and III, in which the ideal LTA topology is preserved, is consistent with our results for all-SiO₂. However, the obtained reversibility from phase IV, in which the LTA topology is lost, is clearly at odds with what we found in the all-SiO₂ case. Note also that, unlike phases V** and VI** of all-SiO₂, phases IV* and IV** of Na-A present coordination defects and are not robustly metastable at low pressures.

Our results for Na-ZK4 (not shown here) can be summarized as follows: (1) At low pressures there are continuous transitions dominated by RUM's. (2) A first-order transition, at 4.25 GPa, causes coordination defects, most of which involve neighboring Si-Al atom pairs that approach to share two O atoms. All the Al atoms in the system give raise to coordination defects, while only a small fraction of the Si atoms do. (3) Upon further compression we find discontinuous transitions to phases in which rings of all types collapse. (4) The second-order transitions are reversible without hysteresis, and all the first-order transitions are irreversible. Thus, as in Na-A, the presence of Al in Na-ZK4 reduces the pressure at which the coordination defects appear. On the other hand, at variance with all-SiO₂ and Na-A, Na-ZK4 does not present any first-order transition to a topology-preserving phase.

Discussion.— Our simulations render a wealth of conclusions that pertain not only zeolites, but PIA phenomena at large. Maybe most importantly, we confirm the existence of the LDA phases reported by Greaves *et al.* [6]. Two of the considered zeolites (all-SiO₂ and Na-A) present an LDA phase, which supports the claim that such phases may be quite common. Further, for all-SiO₂ the LDA phase is predicted to be stable in a wide range of pressures. Our results thus suggest that this zeolite, which has been recently synthesized [13] and is relatively simple, would be ideal for detailed experimental and theoretical studies of the new type of glass proposed in Ref. 6.

Our simulations confirm PIA is a first-order transition, thus supporting the above mentioned nucleation-overwhelms-growth mechanism [5]. In topology-breaking PIA transitions, the structural distortions involve formation of new bonds and, as Fig. 2b suggests, are rather

localized and can freeze in independently from the rest. In the PIA transitions that respect topology, the localized distortions are essentially rigid rotations of the O_4 tetrahedra. This is further confirmed by vibrational calculations showing the *whole* low-energy RUM-related band softens under compression.

The Al atoms facilitate the formation of coordination defects. Such defects are predicted to occur at about 5 GPa in Na-ZK4 and Na-A, which is consistent with experimental data [6, 7], and only above 11 GPa in all-SiO₂. The Na cations, on the other hand, impede the collapse of the rings at whose centers they are located. As a result, there is no formation of new Si–O bonds between atoms on opposite sides of Na-hosting rings. This seems consistent with our finding that Na-A, which contains a large amount of Na, presents an LDA phase while Na-ZK4 does not. Also, based on our results, it seems reasonable to assume large cations will be more effective in preventing rings from collapsing. That is in agreement with reports that, for one particular zeolite, PIA is irreversible for small cations (e.g. H) and reversible for larger ones (e.g. Li and Na). The same rationale applies to the probable role of H₂O molecules preventing PIA [8].

Our results support the CIN picture [5] that topology-preserving PIA transitions are reversible. However, at variance with what is proposed in Ref. 5, they also show that topology-breaking PIA transitions may be reversible. That is the case of Na-A, where the topology breaking is caused by bond formation between atoms that are close neighbors in the crystalline phase. We find in such conditions the coordination defects can be *correctly undone* upon decompression, so that the crystalline structure is recovered. We find the PIA transition to be irreversible in cases in which the coordination defects involve atoms that are away from each other in the crystalline phase (i.e. when the 6M and 8M rings collapse). In such cases, the atoms recover their preferred low-pressure coordination upon decompression, but the resulting ring topology differs from the crystalline one.

Our simulations also refine the CIN picture in what regards the mechanism for irreversibility. According to Ref. 5, irreversibility occurs because the system is *unable* to find the *transition path* to its most stable (crystalline) phase. To some extent our results support such a kinetics-related explanation, as we find that, for amorphous phases with collapsed rings, only a small number of transition paths allow the system to recover both the ideal coordination to first neighbors and the LTA ring structure. However, our work also suggests a second and more important cause for the irreversibility: We find that at high pressures (e.g. above 2 GPa) it is energetically favorable to recover the ideal first-neighbor coordination in ways that break the crystalline ring structure. Thus, in addition to being more numerous, the *wrong* transi-

tion paths (i) are energetically preferred at moderately high pressures and (ii) lead to phases that are robustly metastable at low pressures. This *thermodynamics-related* mechanism constitutes an alternative cause, probably the main one in zeolites, for PIA irreversibility.

We thank J. Junquera for his help with the basis optimization and R.L. Cappelletti for his comments on the manuscript. We thank the financial support of the Spanish Ministry of Science and Education through the “Ramón y Cajal” program, MEC grants MAT2002-02808 (IP) and BFM2003-03372-C03-01 (JI), the Catalan Government grant SGR-2005-683 (JI), and FAME-NoE. We used the facilities of the CESGA supercomputing center.

-
- [1] P. Richet and P. Gillet, *Eur. J. Mineral.* **9**, 907 (1997).
 - [2] J.S. Tse and D.D. Klug, *Phys. Rev. Lett.* **67**, 3559 (1991); N. Binggeli and J.R. Chelikowsky, *Phys. Rev. Lett.* **69**, 2220 (1992); A. Di Pomponio and A. Continenza, *Phys. Rev. B* **48**, 12558 (1993); J.S. Tse and D.D. Klug, *Phys. Rev. Lett.* **70**, 174 (1993); N. Binggeli, N.R. Keskar, and J.R. Chelikowsky, *Phys. Rev. B* **49**, 3075 (1994).
 - [3] J.S. Tse, D.D. Klug, and Y. Le Page, *Phys. Rev. B* **46**, 5933 (1992).
 - [4] J.S. Tse and D.D. Klug, *Science* **255**, 1559 (1992); S.L. Chaplot and S.K. Sikka, *Phys. Rev. B* **47**, 5710 (1993); N.R. Keskar, J.R. Chelikowsky, and R.M. Wentzcovitch, *Phys. Rev. B* **50**, 9072 (1994).
 - [5] M.H. Cohen, J. Íñiguez, and J.B. Neaton, *J. Non-Cryst. Solids* **307-310**, 602 (2002).
 - [6] G.N. Greaves *et al.*, *Nature* **2**, 622 (2003); G.N. Greaves, F. Meneau, O. Majérus, D.G. Jones, and J. Taylor, *Science* **308**, 1299 (2005).
 - [7] Y. Huang and E.A. Havenga, *Chem. Phys. Lett.* **345**, 65 (2001); J. Gulín-González and G.B. Suffritti, *Mic. Mes. Mats.* **69**, 127 (2004).
 - [8] R. Arletti *et al.*, *Am. Min.* **88**, 1416 (2003); E. Fois *et al.*, *Am. Min.* **90**, 28 (2005).
 - [9] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964); W. Kohn and L.J. Sham, *Phys. Rev.* **140**, A1133 (1965); J.P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [10] Regarding SIESTA, see J.M. Soler *et al.*, *J. Phys. Conds. Matt.* **14**, 2745 (2002). We used Troulier-Martins pseudopotentials [*Phys. Rev. B* **43**, 1993 (1991)] and a localized basis with double- ζ and polarization orbitals [basis optimization as in Junquera *et al.*, *Phys. Rev. B* **64**, 235111 (2001)]. We used a 200 Ry real space mesh and only the Γ point for Brillouin Zone integrations.
 - [11] G.T. Kerr and G.T. Kokotailo, *J. Am. Chem. Soc.* **83**, 467 (1961); M.M. Eddy, A.K. Cheetham, and W.I.F. David, *Zeolites* **6**, 449 (1986); J.J. Pluth and J.V. Smith, *J. Am. Chem. Soc.* **102**, 4704 (1980).
 - [12] K.D. Hammonds, M.T. Dove, A.P. Giddy, and V. Heine, *Am. Min.* **79**, 1207 (1994).
 - [13] A. Corma, F. Rey, J. Rius, J.M. Sabater, and S. Valencia, *Nature* **431**, 287 (2003).